Mat. Res. Soc. Symp. Proc. Vol. 740 © 2003 Materials Research Society I7.11

Adhesion of HVOF Sprayed Diamond-Containing Nanostructured Composite Coating

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ABSTRACT

In the present paper mechanical properties of HVOF sprayed diamonds-containing aluminum oxide composite coating have been investigated. Crystallographic and morphologic texture was measured. Diamonds nanoparticles may improve fracture resistance of aluminum oxide-based coating. Investigations of thermally sprayed coatings by the test revealed high accuracy, speed and reliability of the test. It is also thought that the composite coatings will have better thermal conductivity and thermal shock resistance than that of aluminum oxide-based coatings.

INTRODUCTION

Ultra-dispersed diamonds (UDD) are the new synthetic diamond powders produced by chemical purification of explosion products. Nanoparticles of UDD have spherical and isometric form with no crystalline facets and a fractional structure of clusters [1, 2]. They may be presented as a high-dispersed powder. The diamond nanoparticles are being used for many applications because of its highest known hardness, excellent wear resistance and high thermal conductivity.

On the other hand, applications of single diamond-containing coating are still limited because of its poor fracture resistance and adhesion to substrates. Needless to say, fracture and adhesion strength between coating and substrate are the most important parameters to characterize its quality and effectiveness of related technologies. In general, adhesion may determine reliability and durability of the coatings.

Adequate coating-substrate adhesion under service conditions is a prerequisite to the satisfactory performance of any thermally sprayed ceramic-coated-metal system. Were the coating-substrate bond to fail in a given case and detachment of the coating from its substrate to occur as a consequence, the purpose for which the coating was applied would not likely be served. Thus, it becomes plain that the nature of the coating-substrate bond and the mechanisms by which it may fail must be known and understood clearly.

Researches [1-8] indicates that the adhesion generally decays with time at a rate that depends on mechanical loads, temperature and chemical makeup of the environment, the coating porosity, and the state of stress at the coating-substrate interface and within the coating. Moreover, it has been studied [3-14] that adhesive and/or cohesive failure of thermally sprayed ceramic-metal systems proceeds by means of a complex set of rate processes. It follows that investigations of coating-substrate adhesion should be conducted under actual and/or closely simulated service conditions to the extent feasible. This becomes particularly difficult when the coating-substrate system must be subjected to elevated applied load, localized stresses and temperatures during

service; for example, when the coating is to act as a protective wear resistant coating, heat barrier in the hostile, high-temperature environments encountered in advanced energy systems such as bearings, jet engines, or gas turbines.

Objective of the work was to investigate adhesion of thermally sprayed HVOF coatings consisting of dimonds, aluminum oxide and substrate.

TECHNIQUE OVERVIEW

Successful efforts to better understanding of adhesion of thermally sprayed ceramic-coated-metal systems requires an accurate method to measure either the adhesion itself and/or the work of adhesion. There are known simple techniques: a glue-based technique and a pull off-based technique [10, 14-17]. The former is based on pulling out glued together coated samples. The technique may result in rough values of adhesion force. To minimize errors a glue composition should be carefully studied and applied because it may fill pores and voids of a coating. The later, so-called pull-off technique, have been applied in experiments. Ferber [9] observed that mechanical and rheological properties of a medium used to grip a coating significantly affected a measured adhesion value. Alternative technique is based on scratching a coating by a diamond microhardness indenter (or other sharp tool), and/or impacting a coating with a projectile or a hammer. Its application shows that there may be significant regression between experimental data and real adhesion forces because of Van der Waals forces.

In the present researches improved pull-off technique [9] was used to measure an adhesion force of the coatings. Adhesion force was calculated by equation (1) as it follows:

$$\sigma_{adh} = P_H / S = P_H / \left(\pi \cdot R^2\right) \tag{1}$$

Where P_H is force of peeling off a coating [Pa]; mathematical constant π is 3,1415; R is a radius of a ball [m], S is square of an indentation track [m^2].

Microstructure of the coatings was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. XRD measurements were performed on polished samples in a conventional X-ray automatic powder diffractometer (PW-1820 Philips) with a cuata tube, operated at 40 mA and 40 kV. Scans were acquired from 20° to 90° with a step size of 0.025° and exposure times of 4 s per step. The overall chemical composition of the specimens was determined by quantitative energy dispersive X-ray spectroscopy (EDS) measurements in a SEM (JSM 840, Nikon, Japan) equipped with an EDS detector (Model 6506, Micronix, England) which possesses an atmosphere thin window for light element detection ($z > 4$).

A detailed study of the microstructure of the specimen was carried out by conventional TEM using selected area diffraction (SAD). The chemical composition and structure of the phases and grain boundaries were analyzed by analytical TEM and high-resolution TEM. Conventional and analytical TEM were performed on a 200 kV microscope (Model 2000, Pentax, Japan) equipped with an EDS (Model 6506, Micronix, England) and a parallel electron energy-loss spectrometer (peels) detector. High-resolution TEM was conducted on a 300 kV microscope (Model 3010, Nikon, Japan) with a point resolution of less than 0.16 nm. Microhardness was measured with Vickers indentation at load on the indenter of 0.5 N for 30 seconds. Micro-

stresses, grain size and orientation index (texture degree) were calculated. Roughness and microrelief of the coatings were measured by the profilograph-profilometer.

SAMPLES PREPARATION

Steel was substrate of a sample on which alumina-based composite coating containing up to 70% of α-phase of oxide aluminum was produced. Alumina layer has up to 12% pores on the outside of the sample. Diameter of pores ranges from 0.8 to 3.4 μm. The thickness of the alumina-based layer was 300 μm, its microhardness was up to 16 GPa and its Young's modulus was 310 GPa.

Prior to thermal HVOF spraying a base surface was prepared by grinding with water jet contained SiC, oxide aluminum particles with average size of 2 mm. Then surface was preheated. Air consumption was 0.4-0.45 m^3/min. Distance of spraying was between 120 and 140 mm. Thickness of sprayed coating may be up to 3-5 mm.

Table I. Characteristics of ultra dispersed diamonds particles

Principal chemical composition of UDD nanoparticles	82 – 92 % carbon, 1 – 3 % of nitrogen, 1 – 2% of hydrogen, and up to 1 % of other additives.
Phase composition of UDD nanoparticles	80 – 100 % of cubic diamond, 0 – 10 % of hexagonal diamonds, and up to 20 % of diamond as X-ray amorphous carbon.
UDD nanoparticles size	4.0 to 8.0 nm
Size of aggregated UDD clusters	20 - 30 nm
Surface area of UDD nanoparticles	300±30 m^3/gr
Density of UDD nanoparticles	3.1 - 3.2 gr/cm^3
Thermo-stability until oxidation	400 - 450 °C
Thermo-stability until graphitization	1000 - 1100 °C

Ultra dispersed diamonds of 6.0 nm in average size of nanoparticles have been used in experiments to strengthen alumina-based layer. Diamonds were synthesised in strong non-equilibrium conditions of a detonation surge. The diamond nanoparticles look like isometric fragments. Table 1 lists some characteristics of ultra dispersed diamonds.

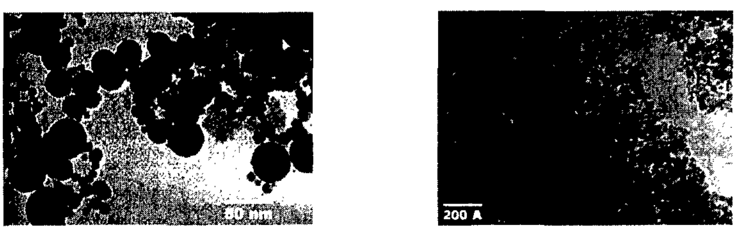
RESULTS & DISCUSSION

Table II shows an effect of UDD nanoparticles on mechanical properties of the composite coating. Diamonds concentration in aluminum oxide-based coating may affect on its size, porosity and roughness (table II). Roughness of the coating decreases up to 0.5-0.3 μm (fig. 1b). Single aluminum oxide structure has generally axial texture. Grains principally orientated in <111> direction.

Table II. Mechanical properties of the aluminum-based diamond containing coating

Thickness from top surface to substrate, μm	Porosity, %	UDD-aluminum oxide phases, %	Roughness, μm	Relative UDD concentration in the coating, %	Size of UDD clusters, nm	Max. hardness, GPa	Internal stress, 10^8 N/m^2	Adhesion, MPa
10	7-12	35-54	2.0-1.0	0.01-0.09	5.10-6.20	12-14	0.06	109.2
20	4-9	34-58	1.4-0.9	0.1-0.34	2.51-3.02	13-17	0.11	123.5
40	5-7	56-63	1.2-0.9	0.5-0.94	3.51-3.81	17-22	0.08	131.8
100	7-9	63-74	1.2-0.9	1.21-2.14	2.12-2.32	21-23	0.146	145.4
200	5-9	51-72	0.55-0.43	1.5-2.3	3.74-3.97	23-25	0.266	124.1
400	4-8	47-71	0.7-0.45	1.7-2.1	4.78-4.99	21-23	0.289	103.8
600	4-8	53-67	0.54-0.39	1.4-1.6	3.84-4.12	20-21	0.278	124.9
800	3-7	54-57	0.75-0.5	1.2-1.8	3.87-4.21	18-23	0.305	124.3
1000	5-6	31-39	0.5-0.3	1.3-1.6	5.72-7.02	12-15	0.333	133.6

UDD nanoparticles increase both internal stresses (up to $0.119 \cdot 10^8$ N/m^2) and microhardness (up to 25 GPa) in all studied cases. UDD nanoparticles are distributed in aluminum oxide-based coating. Nanoclusters (fig. 1a) and single UDD nanoparticles may diffuse into the aluminum oxide-based coating that results in strengthening it. The presence of diamond particles in the composite structure was also indicated by EDS analysis near the surface of the film (fig. 2). Many crystallized centers and clusters of UDD nanoparticles, aluminum oxide hard phases are observed in structure of the coating (fig. 1a,b).



(a) (b)

Figure 1. UDD clusters (a) and nanoparticles (b).

Near the surface of the coating (fig. 2) can be observed strong pudding rocks containing UDD clusters as it is shown at a high-resolution micrograph of diamond nanoparticles. Single UDD nanoparticles and its clusters may conglomerate with aluminum oxide hard phases.

The incident beam was parallel to the <111> axis, with the plane predominantly parallel to the interface. The heavily irradiated region was observed at 10 μm from the surface. High strain and dislocations were observed at thickness of 10-35 μm. However, there was no difference in lattice constants that was distinguished in the Fourier transform (FT) images obtained from the near surface region, damaged region, and deeper-lying region. Presumably, the lattice parameter value was determined to be constant in all studied regions. This may assure that no new original clusters were in the structure.

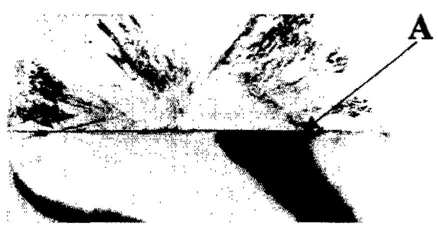


Figure 3. Segment of UDD nanoparticle

Size of the UDD clusters and its distribution in the coating depends on UDD concentration and shape of nanoparticles. Rounded shape of nanoparticles may be invited. In addition, UDD nanoparticles do not affect on HVOF process, but they may affect on mechanism of crystallization and a growth rate of the coating.

CONCLUSION

Ultra dispersed diamond (UDD) nanoparticles effects on roughness, microstructure and hardness of the aluminum oxide-based composites were studied. Roughness decreases up to Ra 0.5-0.3 μm. UDD clusters were found distributed in aluminum oxide-based coating. Hardness of the composite coating is up to 25 GPa at 0.1% UDD concentration; however, UDD nanoparticles may increase internal stresses of the coating. Also UDD nanoparticles may improve adhesion and microhardness of Al_2O_3–based coatings by nanotexturing its structure. Such physical characteristics suggest a number of possible commercial applications for the composite coatings, particularly for wear-resistant and related applications.

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